



D-band center modulation of B-mediated FeS₂ to activate molecular nitrogen for electrocatalytic ammonia synthesis

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ABSTRACT

Electrocatalytic nitrogen fixation is a promising approach for ambient ammonia synthesis. The key that limits the improvement of ammonia evolution performance is the N≡N bond cleavage of molecular nitrogen. One effective route to break this bottleneck is the d-band center modulation of catalysts. Herein, a nonmetal boron mediated FeS₂ (B-FeS₂) is developed for electrocatalytic nitrogen fixation. The B-mediation alters the spin-orbits of Fe site and upshifts the d-band center of FeS₂, thus inducing a strong d-π* interaction between the Fe site and nitrogen to activate N≡N bond. Besides, the experimental and theoretical calculations indicate the B-mediation reduces the energy barrier for *NNH intermediate, thus significantly accelerating ammonia production. As a result, B-FeS₂ displays high ammonia yield (1.56 mmol·g⁻¹·h⁻¹) with 12.6 % Faradaic efficiency. This strategy of d-band center tuning induced by the B-mediation provides a distinctive insight for the design of high-efficiency electrocatalysts.

1. Introduction

Nitrogen reduction for ammonia synthesis driven by the renewable electricity has been considered as an effective method to replace the traditional Haber-Bosch process, due to the benefits of mild reaction conditions and zero carbon emissions [1–3]. However, the molecular nitrogen is difficult to be activated due to the high stability of N≡N triple bond (941 kJ mol⁻¹), thus resulting in the low electrocatalytic nitrogen reduction reaction (eNRR) efficiency [4,5]. One promising route to break this bottleneck is the regulation of the d-band centers of catalysts and the electronic state of the reaction active sites [6,7]. The raised d-band center towards the Fermi energy level of metal-based catalysts enables the formation of the coupling between the d-orbital of metal active site and the p-orbital of nitrogen (Fig. 1), therefore allowing more d-electrons of metal active sites to fill the antibonding state of molecular nitrogen and thus forming a strong d-π* interaction [8–11]. This interaction leads to the significant charge transfer between the molecular nitrogen and the metal active sites of catalysts, therefore accelerating the adsorption process of molecular nitrogen on the surface of catalysts [12]. More importantly, the metal-based catalysts with the higher d-band center and lower work function have the weakened electron binding confinement [13]. This means that the electrons are easier to escape from the surface of the catalysts to fill the antibonding orbitals of nitrogen to activate nitrogen. Therefore, the d-band center

modulation of metal-based catalysts is beneficial to reduce the energy barrier of N≡N triple bond cleavage, facilitate the activation of molecular nitrogen and thus enhance the eNRR performance [14]. For example, Chen et al. [15] reported a strategy to modulate the electronic structure of layered double hydroxide (LDH) by replacing copper with ferrous iron. The introduction of ferrous iron regulates the d-band center position of copper sites in this LDH material, thereby significantly improving the nitrogen adsorption to enhance eNRR activity. Tong et al. [16] constructed Pt₃Fe nanocrystals via the introduction of Fe atoms into the Pt cluster. The Fe-3d band can act as the unique d-d coupling correlation center to upshift the d-band center position of Pt sites and thus facilitate the electron transfer in the Pt 5d orbitals, which significantly improves the eNRR performance of Pt₃Fe (1.02 mmol·g⁻¹·h⁻¹). Ma et al. [17] regulated the binding ability of the reactive sites and nitrogen via introducing metal Zn into Pd, which raised the position of d-band center of the Pd sites. This strategy of optimizing d-band center of Pd sites contributes to an eNRR rate of 0.31 mmol·g⁻¹·h⁻¹ (a Faradaic efficiency of 16.9 %).

Up to now, researches have focused on the d-band center modulation of metal-based catalysts via the introduction of metal heteroatom rather than the non-metal heteroatom [18]. It is worth noting that the non-metal heteroatoms represented by the boron atom have the unique advantages on the d-band center modulation of metal-based catalysts [19]. On one hand, the introduction of the boron heteroatom can trigger

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a strong hybridization between the d orbitals of the metal sites in the catalysts and the p orbitals of the boron atoms, which leads to the emergence of more gap states and the upward shift in the Fermi level of the metal sites of catalysts [20,21]. This change induces a strain in the metal-based catalysts to cause an inhomogeneous distribution of charges, thereby boosting the charge transfer and conductivity of materials [22]. On the other hand, compared to metal mediators, the introduction of non-metal can prevent the formation of the metal-H bonds and the occurrence of hydrogen evolution reaction (HER) to enhance the nitrogen fixation performance [23,24]. Hence, the d-band center modulation by virtue of the boron heteroatom is a promising method to achieve high eNRR activity for metal-based catalysts.

Pyrite (FeS_2) has abundant active sites of nitrogen fixation and can inhibit the competitive reaction of water splitting. However, it does not display satisfactory eNRR performance due to the energy mismatching between the 3d orbitals of Fe sites and the $2\pi^*$ orbitals of N_2 [25,26]. Owing to the characteristics of FeS_2 mentioned above, it can be an appropriate model material for investigating the relation between the d-band center modulation via the boron introduction and the activation of $\text{N}\equiv\text{N}$ bond in nitrogen reduction reaction. In this work, a B-mediated FeS_2 nanosheet is designed and constructed for eNRR. Combined with experiments and density functional theory (DFT), the B-mediation can cause a upshift of the d-band center of FeS_2 to facilitate the activation of $\text{N}\equiv\text{N}$ bond of N_2 and accelerate the first step of hydrogenation in the rate-determining step of eNRR. As a result, the B- FeS_2 shows high ammonia yield ($1.56 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) with 12.6 % FE at -1.4 V vs. Ag/AgCl . This indicates that B-mediated FeS_2 is a promising eNRR catalyst, which is evidenced by the comparison of the advantages and drawbacks with other state-of-the-art eNRR catalysts in Supporting Information.

2. Experimental section

2.1. Synthesis of FeOOH nanosheets

FeOOH nanosheets were prepared via the water-bath method. Specifically, 0.1 M of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and 0.1 M of CH_3COONa were dissolved in 40 mL of H_2O and continuously stirred at 40°C for 2 h to obtain the precursor of FeOOH nanosheets. Then the precursor was washed and dried under 60°C for 12 h.

2.2. Synthesis of Fe_2O_3 nanosheets

Fe_2O_3 nanosheets were obtained via the high-temperature

calcination of the precursor of FeOOH nanosheets. In the typical experiment, the obtained FeOOH nanosheets were placed in a porcelain boat and calcined in a muffle furnace at 300°C for 2 h with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ under the air atmosphere.

2.3. Synthesis of FeS_2 and B mediated FeS_2 nanosheets

The B mediated FeS_2 was prepared by the sulfidation treatment at high temperature in a tube furnace. Typically, 50 mg of Fe_2O_3 , 100 mg of sulfur powder and a certain amount of H_3BO_3 were successively added to the mortar and ground for 5 min. The mixed powder was placed in a porcelain boat and calcined in a tube furnace at 500°C for 2 h under the nitrogen atmosphere. A series of B- FeS_2 samples with the different mass ratios of 200:50, 250:50, 300:50 and 350:50 samples were prepared and labelled as B- FeS_2 -4, B- FeS_2 -5, B- FeS_2 as well as B- FeS_2 -7, respectively. For comparison, the pure FeS_2 was synthesized by the similar synthetic process without the addition of H_3BO_3 , which is labelled as FeS_2 .

2.4. Characterization

The prepared samples were investigated through various instruments. The scanning electron microscope and transmission electron microscope (Talos F200X) equipped with an energy dispersive spectrometer (EDS) were applied to analyze the structure and morphology of obtained samples. Besides, the scanning transmission electron microscope (STEM) was obtained via a FEI Themis Z electron microscope. X-ray diffraction (XRD-6100, SHIMADZU) was used to explore the crystal phases of the as-synthesized samples. The chemical state of the as-prepared samples surface was determined by the time-dependent X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250 spectrometer (Thermo Electron Corporation). The Chemisorption apparatus (Autosorb-iQC-TPX) was used to measure the temperature programmed desorption (TPD) of the synthetic samples. The Brunauer-Emmett-Teller (BET) specific surface areas and pore size were detected by using the Barrett-Joyner-Halenda (BJH) methods.

2.5. Electrode preparation

In a typical experiment, 6 mg of the as-prepared catalyst was added to 1 mL of ethanol contained 5 vol% Nafion solution. And the mixture was sonicated for 20 min to obtain a homogeneous slurry. Subsequently, 50 μL of the prepared slurry was loaded on a carbon paper (1 cm^2) electrode and dried.

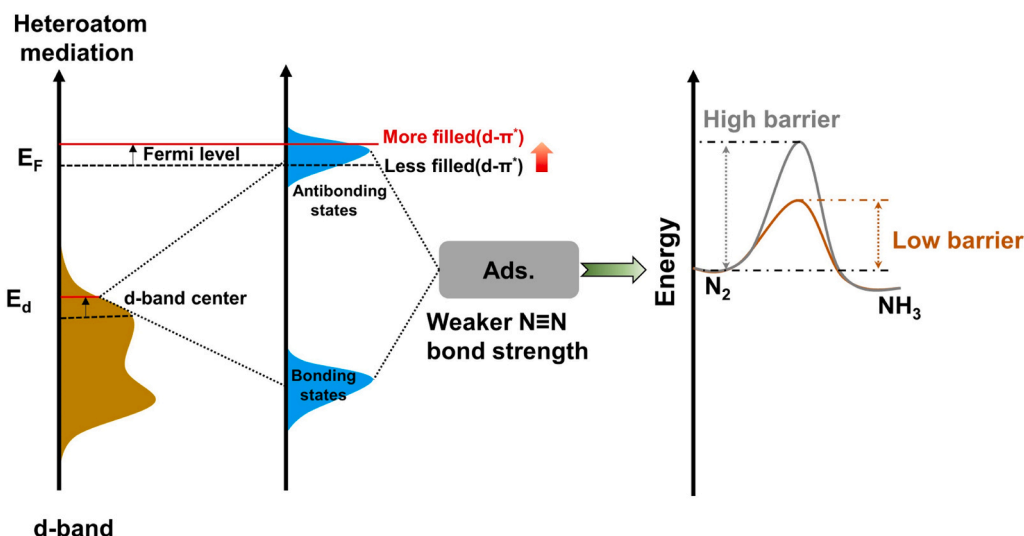


Fig. 1. The mechanism diagram of the upshifting of the d-band center related to metal-based catalysts for boosting nitrogen reduction.

2.6. Electrochemical measurement

All tests were investigated by the electrochemical analyzer (AME-TEK, PMC-1000/DC) with a standard three-electrode system. For the electrochemical active surface area (ECSA) test, the prepared electrode served as the working electrode, while an Ag/AgCl electrode (3 M KCl) was used as the reference electrode. A carbon rod was employed as the counter electrode, and the methanol solution of 0.1 M KOH was used as the electrolyte. For the electrochemical impedance test, 1 mg of catalyst was added to 200 μ L of ethanol contained 10 vol% Nafion and sonicated for 30 mins. Then the solution mentioned above was loaded on ITO glass as the working electrode, Ag/AgCl (3 M KCl) electrode was used as the reference electrode. Carbon rod was used as the counter electrode, and the 1 M Na₂SO₄ solution was used as the electrolyte.

2.7. Electrocatalytic nitrogen reduction reaction

The electrocatalytic nitrogen reduction reaction was conducted in a H-type cell applied as the electrolytic tank. Firstly, the cathode and anode of the H-type cell were added with 30 mL of 0.1 M KOH methanol solution containing 0.16 vol% H₂O, and the absorption solution consisted of 30 mL of 0.1 M HCl. Subsequently, the pure N₂ gas was purged into 100 mL of 1 M H₂SO₄ and 100 mL of 1 M KOH to remove potential NO_x and NH₃. Finally, the nitrogen was fluxed into the H-type cell for 30 min to reach saturation in the electrolyte before electrocatalytic testing. As a contrast, the blank experiment follows the similar process in Ar atmosphere.

The Faradaic efficiency (FE) of the as-prepared samples were investigated under the same experimental conditions as above. The FE for ammonia was calculated using the following equation $FE = (3F \times n \times V) / (17 \times Q)$, where F represents the Faraday's constant, n is the concentration of ammonia generated, Q represents the amount of charge, and V represents the volume of electrolyte. Three independent tests were carried out to calculate the error bars of the eNRR activity.

2.8. Determination of ammonia production

The ammonia produced was quantitatively detected by the common spectrophotometric indophenol blue method. Briefly, the electrolytic solution after the cathodic electrolytic cell reaction and the adsorbing solution were mixed and rotary evaporated to obtain NH₄Cl product. After that, 10 mL of ultrapure water was added to obtain a product solution. Then, a indophenol blue method was used to measure the ammonia content. Concretely, the NaOH solution containing 5 wt% sodium citrate and 5 wt% salicylic acid (2 mL), 0.5 M NaClO solution (1 mL) and 1 wt% Na₂[Fe(CN)₅NO] solution (0.2 mL) were sequentially added to 2 mL of the sample to be tested, which was shaken, left to stand in a dark place for 2 h, and then its absorbance at a wavelength of \sim 657 nm was measured via UV-vis diffuse reflection spectra. The ammonia content was calculated by the absorbance of a series of standard liquids with different concentrations of ammonia. The ammonia yield was calculated as following: $r = (c \times v) / (t \times m)$, where c is the concentration of ammonia produced (mol·L⁻¹), v represents the volume of the product solution (L), t is the reaction time (h), and m is the catalyst content (g).

2.9. Determination of hydrazine hydrate

The possible by-product of N₂H₄ can be measured by the Watt and Chrisp method. In a typical experiment, 300 mL of ethanol, 30 mL of concentrated hydrochloric acid and 5.99 g of p-C₉H₁₁NO were used to obtain the color reagent. The 5 mL of the product solution was mixed with the 5 mL of as-prepared color reagent and stayed at room temperature for 20 mins. If the N₂H₄ was generated in the reaction solution, it can react with the p-C₉H₁₁NO to form a yellow azo compound under

the acidic conditions. More importantly, the absorbance of the mentioned azo compound containing N₂H₄ can be recorded at a wavelength of \sim 455 nm in the UV-visible diffuse reflectance spectra (DRS). The content of the generated N₂H₄ was quantitatively calculated according to the standard curve of N₂H₄ at in the UV-visible DRS.

2.10. In-situ FTIR

A Pt wire was used as the counter electrode, Ag/AgCl as the reference electrode, and the ink of catalyst was coated on the glassy carbon electrode as the working electrode. Electrochemical in-situ FTIR was carried out by a Bruker INVENIO FTIR spectrometer equipped with an MCT detector and a CaF₂ light window via the external reflection mode. Before the test, the high purity nitrogen was aerated for half an hour in nitrogen-methanol co-electrolysis system to reach nitrogen saturation. All the spectra were scanned for 16 times. All backgrounds were acquired without the applied external potential.

2.11. DFT calculation

The first-principles calculations were realized through the Vienna Ab Initio Simulation Package (VASP). To describe the effects of exchange correlation and on-site Coulomb interactions, we utilize a generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) in VASP with Hubbard + U correction. Where the U_{eff} value is 2 eV and is described as van de Waals using empirical corrections in the Grimme scheme (DFT + D2). The plane wave cut-off energy is 520 eV. The Cubic FeS₂ with the space group of Pa-3 (205) was used. The calculation model consists of 72 atoms. The convergence criteria for the total energy and the Hellmann-Feynman force are 10⁻⁷ eV and 0.02 eV·Å⁻¹, respectively. In order to accurately describe the electrons and magnetism of FeS₂, its antiferromagnetic structure has been considered, using MAGMOM of 4. And combined with XRD and HRTEM analysis, the exposed (200) plane of FeS₂ lattice was used as the reaction surface. A Monkhorst-Pack 5 × 5 × 1 k-point grid was utilized to sample the Brillouin zone with a vacuum thickness of 25 Å. The proton-coupled electron transfer (PCET) technique is used. The computational hydrogen electrode (CHE) model is used as the reference for all Gibbs free energy values. The H⁺/e⁻ pair is considered to have a half as much chemical potential as the H₂ gas molecule. The formula for calculating gas pressure is $G = E + ZPE - TS$, where E is the reaction energy difference between products and reactants that occurs on the catalyst. When the vibrational frequency is considered, ZPE and S represent the zero-point energy and entropy changes at 298.15 K, respectively.

3. Results and discussion

3.1. Morphology and crystal phase structure of catalysts

The synthesis process of B-mediated FeS₂ is obtained via a two-step calcination method (Fig. 2a). During the sulfidation process, the part of S atoms were replaced by B atoms to form Fe-B bond in FeS₂, thereby obtaining B-mediated FeS₂. The morphology of B-FeS₂ was analyzed by SEM, STEM and TEM. As shown in Fig. 2b and Fig. S1c, both B-FeS₂ and FeS₂ exhibit the typical nanosheet microstructure, which are similar in the structure of the precursors of FeOOH and Fe₂O₃ (Fig. S1a,b and Fig. S2). Fig. 2c shows the high-resolution TEM (HRTEM) image of B-FeS₂. It could be clearly observed that the lattice distance of B-FeS₂ is 0.271 nm, belonging to the (200) crystal plan of the cubic FeS₂. The corresponding energy dispersive spectra (Fig. 2d) of B-FeS₂ confirmed that S, Fe and B elements are uniformly distributed in space, suggesting of the successful construction of boron in the FeS₂ nanosheets. The content of B in FeS₂ is 0.8 wt% through inductively coupled plasma mass spectrometry (ICP-MS) (Table S1).

The phase and crystal structure of as-prepared samples were investigated by X-ray diffraction (XRD). As shown in Fig. 2e and Fig. S3a, all

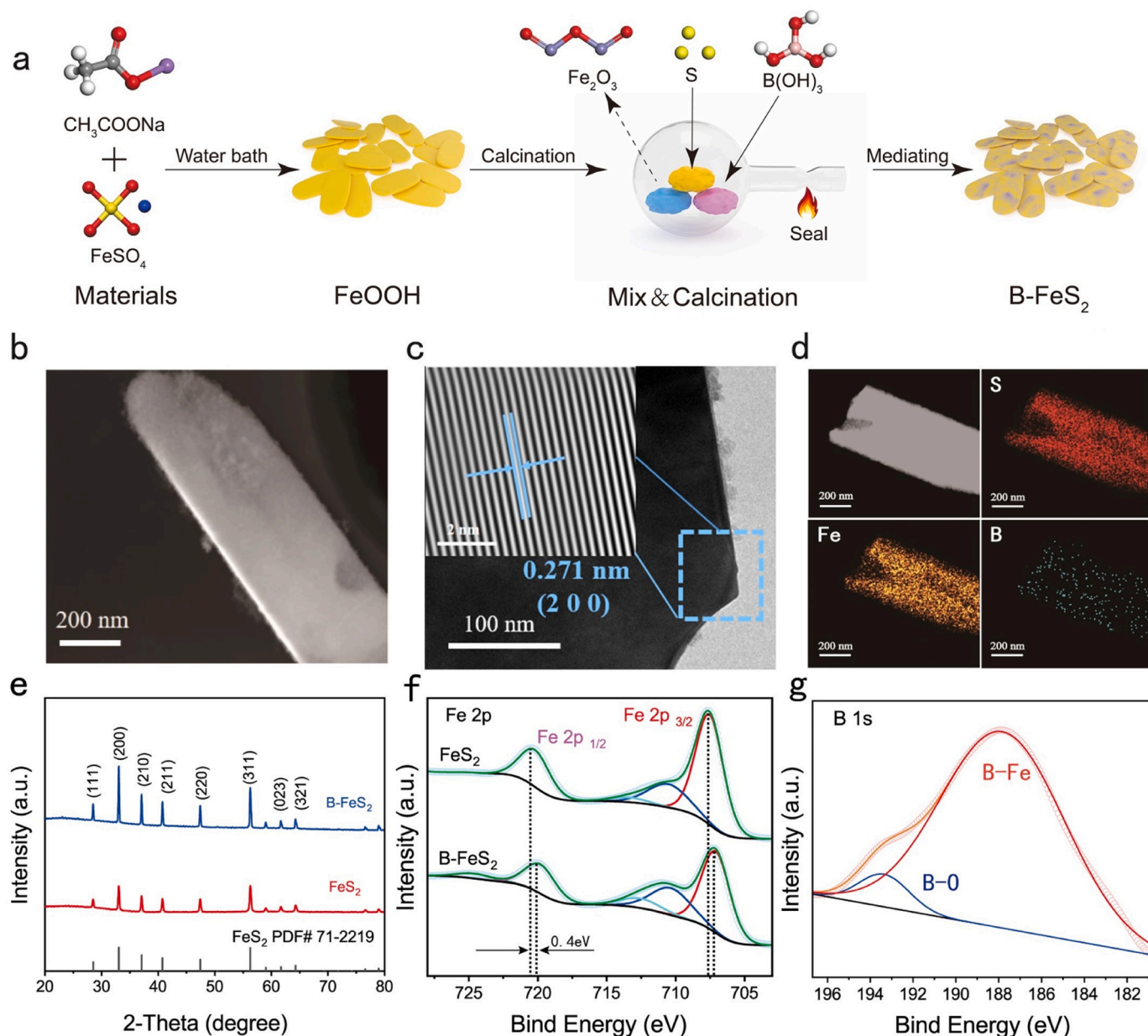


Fig. 2. (a) Schematic diagram of the preparation process for B-mediated FeS₂ nanosheets. (b) TEM, (c) HRTEM and (d) TEM images of the B-FeS₂ and the corresponding mapping images of the elements of S, Fe and B, (e) XRD patterns of the FeS₂ and B-FeS₂. The XPS spectrum of samples (f) Fe 2p and (g) B 1s.

XRD peaks belong to the cubic FeS₂ (JCPDS, No. 71-2219). Notably, the XRD peaks of B-FeS₂ are more sharp than of FeS₂, indicating the improved crystallinity due to the introduction of B element. Besides, by contrast with FeS₂, the XRD peaks of B-FeS₂ are shifted to the high-angle direction with the increased content of B (Fig. S3b). This is because the B atoms with the relatively small atomic radius replace some of S atoms in FeS₂. Additionally, to further investigate the electronic structure of the B-FeS₂ catalyst, the chemical state of the surface of B-FeS₂ and pure FeS₂ were characterized by X-ray photoelectron spectroscopy (XPS). As displayed in Fig. S4, the two characteristic peaks at 162.6 eV and 163.9 eV in the S 2p region of pure FeS₂ correspond to S 2p_{3/2} and S 2p_{1/2}, respectively. However, the two peaks at 162.3 eV and 163.6 eV of B-FeS₂ are ascribed to S 2p_{3/2} and S 2p_{1/2}, respectively, which shifted 0.3 eV to the low binding energy compared with that of pure FeS₂ owing to the B introduction [27]. For Fe 2p region (Fig. 2f), the XPS peaks of B-FeS₂ at 707.3 eV and 720.1 eV belong to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The lowered binding energy compared with pure FeS₂

(707.7 eV, 720.5 eV) is due to the mediation of low-electronegativity B, which enables the adjacent Fe atoms to show the electron-rich state [28]. As shown in Fig. 2g, the faint peaks were detected in B-mediated FeS₂, which is related to B 1s. Besides, the peaks at 187.8 eV and 193.1 eV correspond with Fe-B bond in B-FeS₂, further confirming the successful mediation of B into FeS₂ nanosheets [29,30].

3.2. Electrocatalytic nitrogen reduction performances of catalysts

The eNRR performances of samples were investigated in an H-type electrolytic cell with the nitrogen-saturated electrolyte. The nitrogen-methanol co-electrolysis system was used to significantly reduce the overpotential of the anodic reaction (Fig. S5). The generated NH₄⁺ was measured spectrophotometrically with the indophenol blue and quantified by the calibration NH₄⁺ curve (Fig. S6). The eNRR performances of B-mediated FeS₂ catalysts with different B amounts were investigated in Fig. S7 to find out the best sample with the optimal B content. As shown

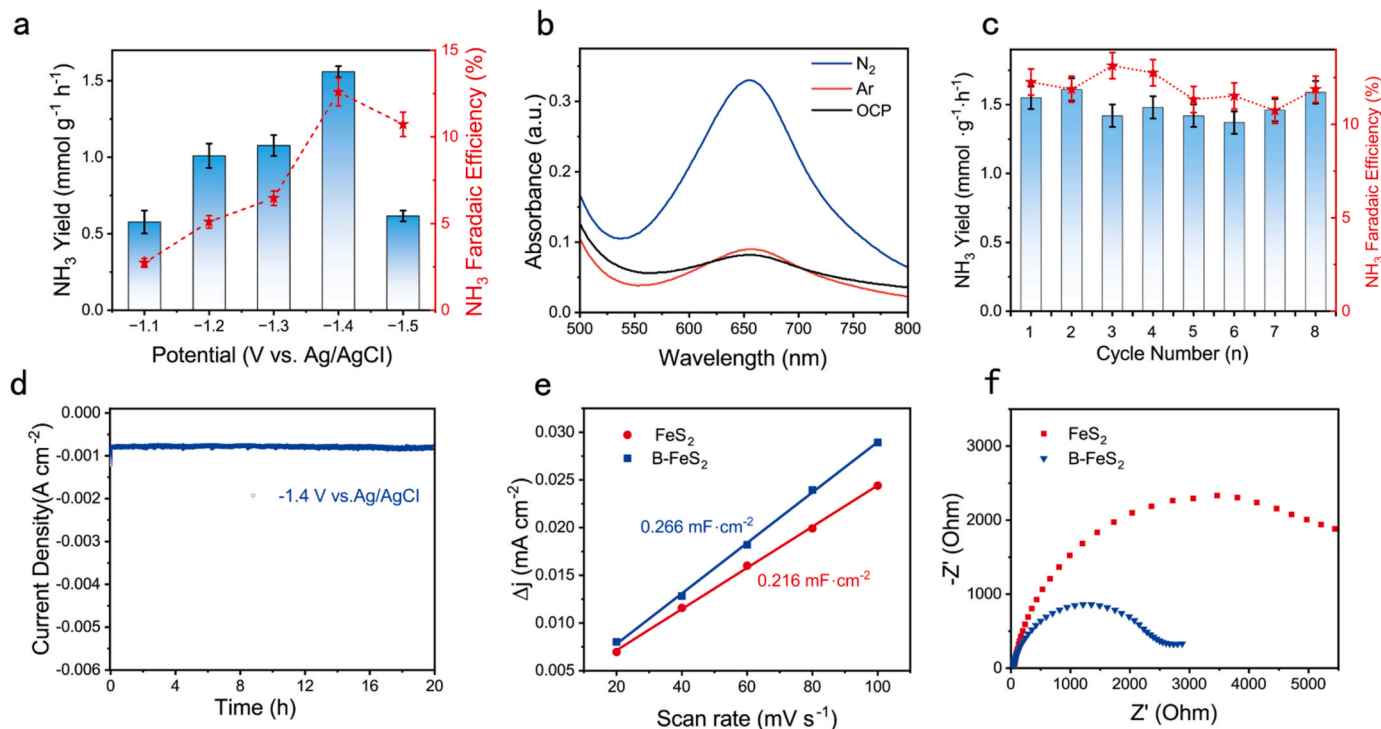


Fig. 3. (a) Ammonia yield and Faradaic efficiency of B-FeS₂ at different potentials. (b) Absorbance of B-FeS₂ in UV-Vis spectra under nitrogen, argon and open circuit potential (OCP) conditions. (c) Cyclic stability, (d) Time-dependent current density of B-FeS₂ at -1.4 V vs. Ag/AgCl. (e) The ECSA, (f) EIS Nyquist plot of B-FeS₂ and pure FeS₂ catalysts.

in Fig. 3a and Fig. S8, the eNRR rate of the optimal B-FeS₂ sample reached 1.56 mmol g⁻¹ h⁻¹ with a Faradaic efficiency of 12.6 % at -1.4 V vs. Ag/AgCl, outperforming many reported catalysts (Table S2). The outstanding eNRR performance of B-FeS₂ is evidenced by linear sweep voltammetry curves (Fig. S9). Besides, this conclusion is also proved by the activity tests of B-FeS₂ in the Ar atmosphere and open-circuit potential (Fig. 3b). As expected, NH₃ was formed only under nitrogen, suggesting that the source of generated ammonia in the electrolyte is derived from nitrogen. Stability is an important factor in evaluating catalyst performance. In Fig. 3c and Fig. S10, the prepared B-FeS₂ catalyst showed no significant decrease in ammonia yield and Faradaic efficiency after the eight cycle tests. In addition, as shown in Fig. 3d, the current density has no obvious decay after the 20 h eNRR reaction, indicating the good stability of the B-FeS₂ catalyst, as evidenced by the XRD pattern of B-FeS₂ after the reaction (Fig. S11).

The eNRR performance is directly related to the reactive sites of the catalysts. The reactive sites determine the amount of nitrogen adsorption activation, and the Electrochemical Active Surface area (ECSA) can directly reflect the number of catalytic active sites. The ECSA of B-FeS₂ and pure FeS₂ were obtained via the Cyclic Voltammetry (CV) at different scanning speeds (Fig. S12). And as shown in Fig. 3e, compared with pure FeS₂ (0.216 mF·cm⁻²), the ECSA value of B-FeS₂ can reach up to 0.266 mF·cm⁻², indicating that the B mediation can induce more active sites to participate in the reaction, thereby enhancing the eNRR performance. In addition, the adsorption and desorption isothermal curves of nitrogen were tested. As displayed in Fig. S13 and Table S3, B-FeS₂ shows the larger specific surface area and increased pore volume compared with pure FeS₂. It is because the precursor decomposition of H₃BO₃ at high temperatures can produce gas to cause the increased specific surface area of B-FeS₂. Additionally, the charge transfer resistance of catalysts is revealed by the electrochemical impedance spectroscopy (EIS). As shown in Fig. 3f and Fig. S14, the charge transfer resistance of B-FeS₂ was significantly decreased than that of FeS₂, suggesting the boosted charge transfer capability induced by the introduction of B atoms [31–33].

Besides, the nitrogen adsorption capacity of catalysts was detected by temperature programmed desorption isotherms (TPD) under N₂ atmosphere. As displayed in Fig. S15a, the chemical desorption temperature of B-FeS₂ is 557 °C, which is higher than that of pure FeS₂ (540 °C), indicating that B-FeS₂ requires a higher temperature to surmount the desorption of N₂ [34]. In addition, the TPD of NH₃ was also examined. As in Fig. S15b, the desorption temperature of B-FeS₂ for ammonia is lower than that of pure FeS₂, manifesting that B-FeS₂ can desorb the product ammonia in time to release the active sites. Moreover, the adsorption energy of nitrogen on B-FeS₂ and pure FeS₂ were calculated by DFT. As shown in Fig. S16, the adsorption energy of B-FeS₂ for nitrogen is -1.15 eV, which is higher than that of pure FeS₂ (-0.88 eV). This indicates the strong nitrogen adsorption energy of B-FeS₂, corresponding to the N₂-TPD conclusion.

3.3. The influence of d-band center modulation for B-FeS₂ on the generation of intermediates and eNRR performance

To explore the action of d-band center modulation on the generation of intermediates in eNRR process, the catalytic pathway of B-FeS₂ was investigated through in-situ FTIR spectroscopy. As shown in Fig. 4a, the intensity of the characteristic peaks related to -N-N and -N=N bonds becomes stronger with the increasing reaction time during the eNRR process, revealing the cleavage of the N≡N bond on the surface of catalyst [35,36]. The peaks at 1330 cm⁻¹, 1520 cm⁻¹ and 1420 cm⁻¹ were attributed to the characteristic peaks of adsorbed NH₃ and asymmetric deformation vibrations of NH₄⁺, respectively, suggesting the generation of ammonia in the eNRR process [37]. In addition, the characteristic peaks at 1090 cm⁻¹ and 1620 cm⁻¹ were attributed to the vibrations of the intermediate -NH₂ and -N-H in the eNRR process, respectively [38,39]. Moreover, the in-situ FTIR spectroscopy of pure FeS₂ was also tested under the same conditions. As shown in Fig. S17, the intensity related to the peaks of intermediates and produced ammonia in B-FeS₂ is significantly higher than that of pure FeS₂, suggesting that B-FeS₂ can produce more intermediates under the eNRR

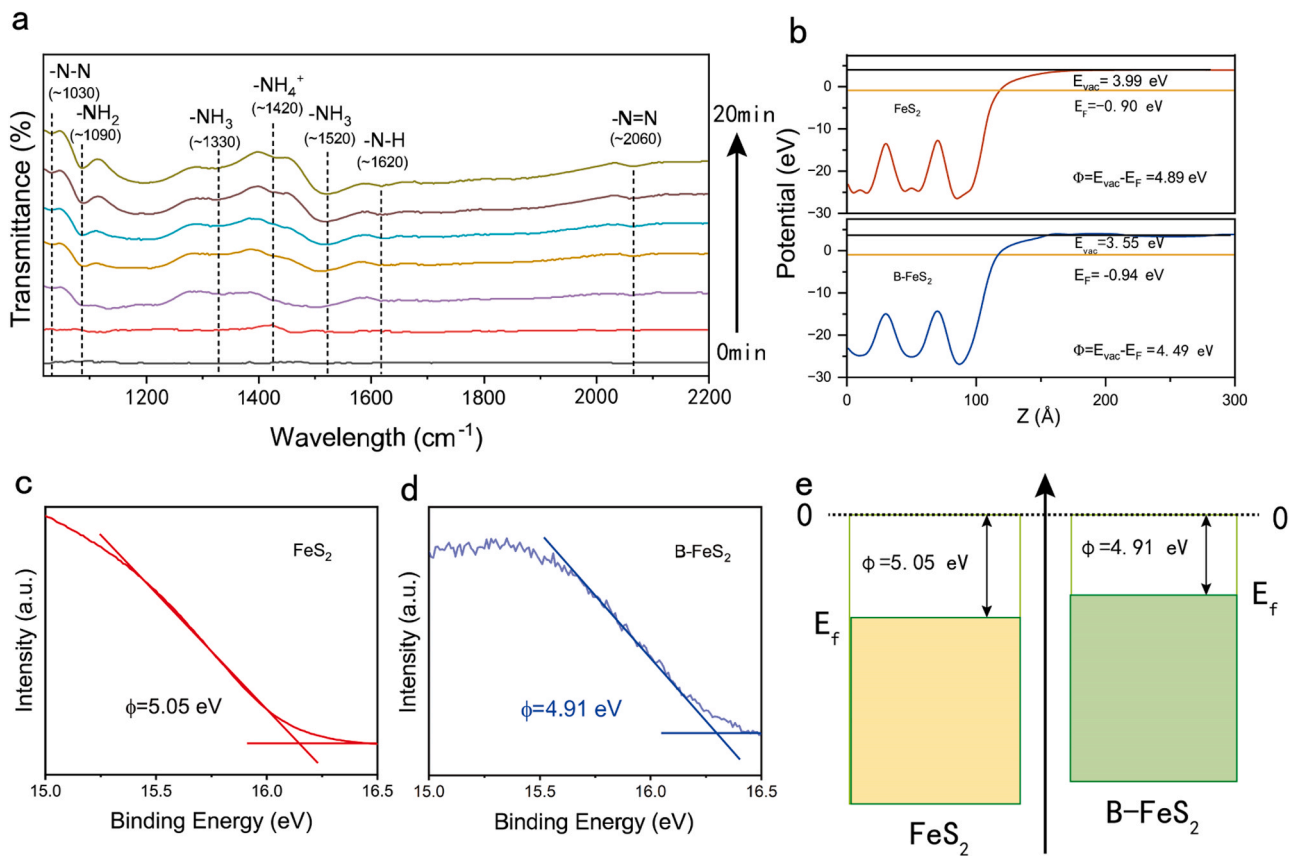


Fig. 4. (a) In-situ FTIR spectra of B-FeS₂. (b) The corresponding work functions of FeS₂ and B-FeS₂ calculated by DFT. UPS spectra corresponding to the work function of (c) Pure FeS₂ and (d) B-FeS₂. (e) The schematic of the work functions of pure FeS₂ and B-FeS₂.

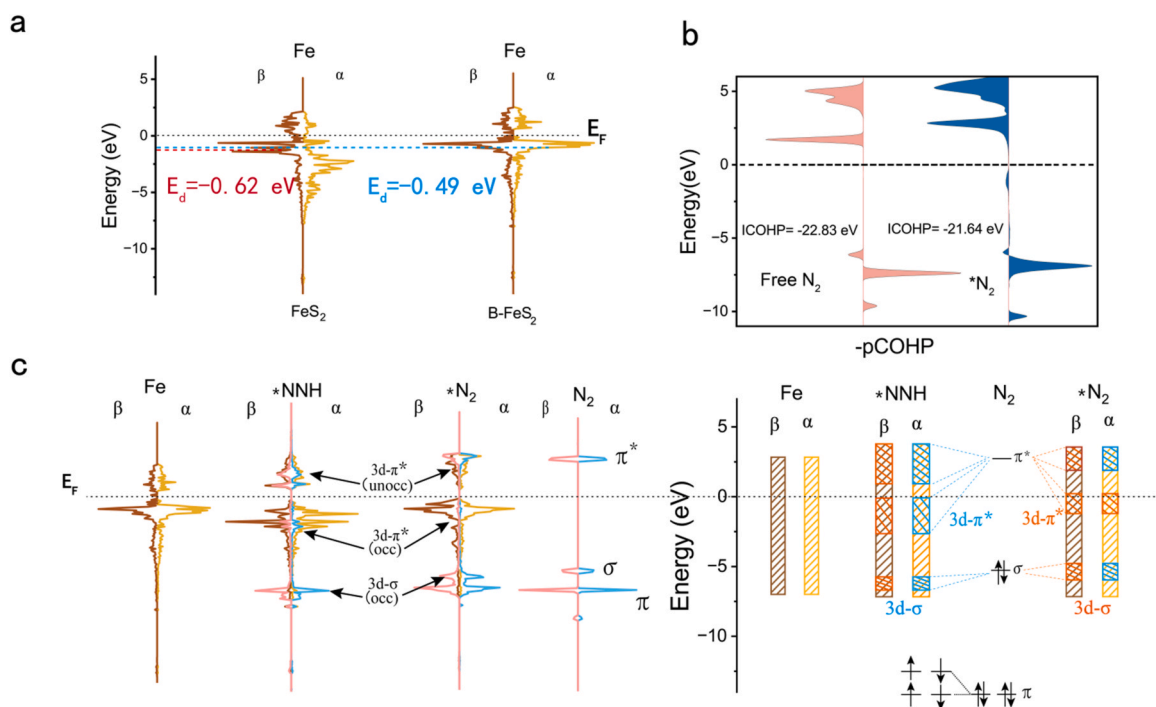


Fig. 5. (a) Projected electronic densities of states (PDOS) related to 3d orbitals and d-band center of the Fe sites over pure FeS₂ and B-FeS₂. (b) The computed pCOHP of free N₂ and *N₂ on B-FeS₂. (c) PDOS related to the interaction between the d orbitals of the Fe sites and the nitrogen molecules.

process. This phenomenon strongly evidences that the eNRR kinetics of B-FeS₂ is faster than that of FeS₂ due to the raised d-band center of Fe sites [40], which is beneficial to improve the eNRR activity.

To further illustrate the relationship between the B mediation and the change in the d-band center of FeS₂, the work function of FeS₂ and B-FeS₂ were calculated by DFT calculations. As displayed in Fig. 4b, the work function of B-FeS₂ (4.49 eV) was lower than that of FeS₂ (4.89 eV) calculated by DFT. This conclusion is proved by the ultraviolet photoelectron spectroscopy (UPS). As displayed in Fig. 4c,d and Fig. S18, the work function of B-FeS₂ is 4.91 eV, while the work function of pure FeS₂ is 5.05 eV. These indicate that B mediation can effectively reduce the work function of FeS₂, thus leading to a higher Fermi energy level and d-band center energy level of B-FeS₂. Combined with the experimental and calculation results presented above, the lowered work function of B-FeS₂ suggests the higher E_d energy level compared with FeS₂. This indicates that the binding energy of high-energy electrons regarding the Fe sites in B-FeS₂ become weak, so more high-energy electrons can participate in the eNRR reaction (Fig. 4e).

To explore the reason that B mediation can upshift the d-band center of FeS₂, we carried out the theoretical calculations on the projected electronic densities of states (PDOS) related to the 3d orbitals of Fe sites in pure FeS₂ and B-FeS₂. Fig. 5a shows that the B atoms mainly modulate the spin-up electronic state of the Fe sites, and the spin-up electrons shifted up nearly to the Fermi energy level of FeS₂, thus mediating the d-band center of B-FeS₂. Furthermore, the PDOS also shows that the d-band center of pure FeS₂ is -0.62 eV, while the d-band center of B-FeS₂ is -0.49 eV, manifesting an upshift of 0.13 eV from FeS₂ to B-FeS₂. To investigate the effect of the raised d-band center on the nitrogen activation, the projected crystal orbital Hamilton population (pCOHP) of B-FeS₂ was studied. As exhibited in Fig. 5b, the bonding contribution is on the right while the antibonding contribution is on the left. It is clearly shown that the antibonding orbitals of free nitrogen near the Fermi level are not filled with electrons, but the antibonding orbitals of nitrogen adsorbed on surface of B-FeS₂ near the Fermi level display obvious electron filling states, suggesting that nitrogen is activated. Additionally, compared with free nitrogen (22.83 eV), the absolute ICOHP value related to the nitrogen adsorbed on surface of B-FeS₂ (21.64 eV) is lower, suggesting that the electrons of B-FeS₂ can effectively transfer to the antibonding orbitals of nitrogen to activate N₂ [41].

Furthermore, according to the d-band center theory, when the chemisorption occurs on the metal sites, the d orbitals of the metal sites can interact with the adsorbed reactant molecules to form the bonding and antibonding states. The position of the d-band center determines the extent to which the antibonding states are filled with electrons, which in turn determines the stability of the bonding and the strength of the adsorption. As shown in Fig. 5c, the 3d orbital of Fe can match with the π^* orbital of nitrogen, thus forming the partially occupied 3d- π^* (occ) orbitals. With the construction of these 3d- π^* orbitals, the electrons from Fe 3d orbital can transfer to the empty π^* orbital of the nitrogen, therefore activating the N≡N bond of N₂. Moreover, other formed unoccupied 3d- π^* (unocc) antibonding orbitals located above the Fermi energy level leading to the increased adsorption strength of N₂ for the Fe sites in B-FeS₂. After the N₂ is effectively activated, the *N_2 can react with H⁺ in reaction solution to form *NNH , the 3d orbitals of Fe overlap with the π^* orbitals of *NNH , thus further weakening the N≡N triple bond of N₂ [42,43]. In addition, the 3d- σ (occ) orbital bonding state is about 0.15 eV, which is smaller than the δ orbital of the nitrogen, indicating that the nitrogen is further activated. As a result, in the subsequent continuous hydrogenation process, Fe and H atoms can continuously provide electrons to the empty π^* orbitals of nitrogen, therefore facilitating the process of nitrogen hydrogenation to ammonia production.

3.4. The eNRR mechanism of catalysts

To further demonstrate the nitrogen activation by Fe sites. The

electron localization functions (ELF) and charge density differences related to nitrogen adsorption on the Fe sites were examined. Compared with nitrogen adsorbed onto pure FeS₂ (Fig. S19), the negative charges are mainly concentrated on the adsorbed nitrogen molecules, thus forming a significant charge accumulation in Fig. 6a [44,45]. In addition, there is charge transfer between the Fe sites and nitrogen molecules, which indicates that the Fe site transfers electrons to the empty π^* orbital of N₂ (Fig. 6b process 1). Besides, the lone pair of electrons from nitrogen is injected into the empty d orbital of Fe (Fig. 6b process 2), thus activating the N≡N bond and boosting the eNRR performance. Additionally, Bader Charge of the Fe sites in pure FeS₂ and B-FeS₂ was calculated (Fig. S20). After the B mediation, the Bader Charge of Fe sites changed from 0.645 |e| to 0.502 |e|, suggesting that the B atoms modulate the electronic structure of Fe to the electron-rich state, which is consistent with Fig. 2f. Besides, the Bader Charge of the dinitrogen molecule and the bond length for N≡N triple bond were calculated during the eNRR hydrogenation according to the alternating path. As shown in Fig. 6c, the Bader Charge of the dinitrogen molecule adsorbed on FeS₂ ($^*N_2 + H^+ + e^- = ^*NNH$) is 0.351 |e|, while the Bader Charge on B-FeS₂ increases significantly to 0.499 |e|, demonstrating that the dinitrogen molecule is well activated on B-FeS₂ [46]. In addition, the bond length of the dinitrogen molecule also changed from 1.186 Å to 1.219 Å in Fig. S21, which is favorable for the following eNRR process.

The eNRR reaction mechanism of nitrogen on FeS₂ and B-FeS₂ was investigated. The complex mechanism indicates that the eNRR reaction is a multi-step electron-coupled proton process. As shown in Fig. S22, the adsorption of nitrogen molecule on the surface of FeS₂ and B-FeS₂ is a spontaneous process. Furthermore, when comparing the distal pathway with the alternating pathway, there is a significant uphill energy barrier ($^*NNH_2 + H^+ + e^- = ^*N + NH_3$) for the pure FeS₂ and B-FeS₂ systems in the distal pathway. This suggests that the pure FeS₂ and B-FeS₂ systems face huge challenges in the following distal pathway during eNRR process from the thermodynamical respect. Consequently, the eNRR reaction on both FeS₂ and B-FeS₂ is inclined to occur via the alternating pathway. Moreover, as displayed in Fig. 6d, compared with pure FeS₂ (-0.337 eV), nitrogen is more readily adsorbed on B-FeS₂ due to the lower adsorption energy (-0.501 eV), corresponding with Fig. S15 and Fig. S16. It is noteworthy that the first hydrogenation step ($^*N + H^+ + e^- = ^*NNH$) exhibits the highest energy barrier in the eNRR processes over pure FeS₂ and B-FeS₂. This indicates that the first hydrogenation step is the rate-determining step (RDS) for the eNRR route. Furthermore, to verify this conclusion, the proton source in the electrolyte was replaced by D₂O, the eNRR performance and LSV curves are shown in Fig. S23. It can be observed that a significant decrease trend occurs on the eNRR performance, FE as well as the current density after the replacement of water by D₂O. This is due to the difference in the mass of H/D and the vibration frequency of the bond [47]. The kinetic isotope effect (KIE) value of B-FeS₂ is about 3.18, which is consistent with the characteristics of primary KIE [48]. These results indicate that B-FeS₂ significantly accelerates the activation of N₂ and the first step of hydrogenation [49]. Nevertheless, B-FeS₂ exhibits a markedly different value of ΔG (0.519 eV) in the first hydrogenation step compared with pure FeS₂ (1.201 eV), resulting in the energy barrier of B-FeS₂ is relatively lowered by 0.682 eV. It is because B-FeS₂ can transfer more d electrons to the antibonding orbitals of nitrogen and elongate the nitrogen-nitrogen triple bond (Fig. 6c and Fig. S21), thus effectively activating nitrogen molecule and lowering the energy barrier for the eNRR process. Moreover, The intermediate N₂H₄ was experimentally detected by the spectrophotometric experiment to verify the reaction pathway [50]. The N₂H₄ intermediate was detected in the electrolyte after 2 h reaction over B-FeS₂ (Fig. S24 and Fig. S25), suggestive of an alternating pathway occurred (Table S4).

According to all results presented above, the B-mediation alters the spin-orbits of Fe site and upshifts the d-band center of FeS₂, therefore inducing a strong d- π^* interaction between the Fe site and nitrogen to activate N≡N bond. Moreover, the experimental and theoretical

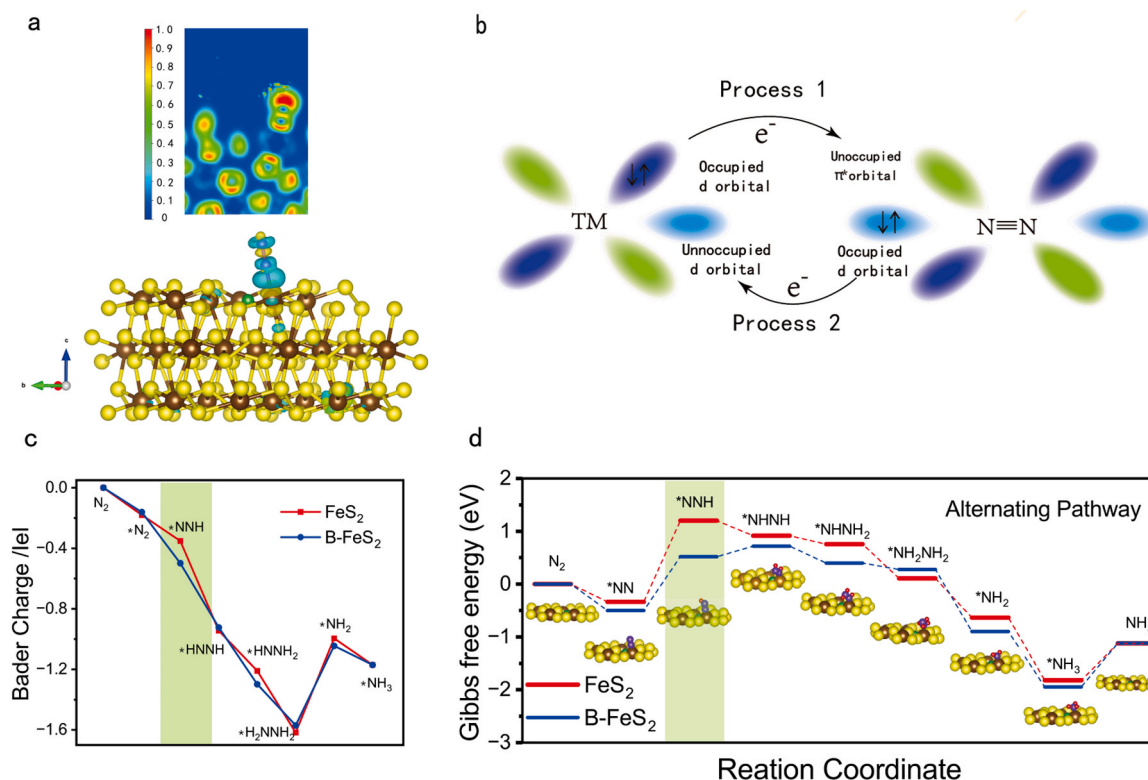


Fig. 6. (a) Electronic location function (ELF) and Charge density differences (Yellow implies charge accumulation and blue implies charge depletion; brown sphere: iron atom, green sphere: born atom, yellow sphere: sulfur atom, and blue sphere: nitrogen atom) of nitrogen adsorbed on the B-FeS₂. (b) Schematic diagram of electron transfer between nitrogen and Fe sites. (c) Bader Charge of dinitrogen molecules on FeS₂ and B-FeS₂. (d) Calculated free-energy diagram for alternating pathways on B-FeS₂ and FeS₂.

calculations reveal that the B-mediation can facilitate the first-step hydrogenation of N₂ in the RDS of eNRR via reducing the energy barrier for *NNH intermediate. Therefore, B-FeS₂ shows a high ammonia yield (1.56 mmol·g⁻¹·h⁻¹) with 12.6 % Faradaic efficiency at -1.4 V vs. Ag/AgCl. This strategy of d-band center mediation via the B atoms is an effective means to activate the reactant molecules and thus boost the catalytic activity. It can be applied to a lot of reactions to acquire the high-yield products except for eNRR, such as hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO₂RR), electro-oxidation reaction (EOR), and oxygen evolution reaction (OER), etc.

4. Conclusions

In conclusion, we designed a B-mediated FeS₂ as an efficient eNRR electrocatalyst via the modulation of d-band center. DFT theoretical calculations and experiments showed that the B-mediation can upshift the d-band center of FeS₂ nearly to the Fermi energy level. As a result, a strong d-π* interaction between the π* orbitals of nitrogen molecules and the 3d orbitals of the Fe sites occurred, thus contributing to a high eNRR rate of 1.56 mmol·g⁻¹·h⁻¹ and a FE of 12.6 % for B-FeS₂, outperforming most of eNRR catalysts. This work provides a new insight for the design of eNRR catalyst through the d-band center modulation.

CRediT authorship contribution statement

Hang Xiao: conceptualization, methodology, writing–review & editing. Mengyang Xia: validation, data curation, formal analysis. Ben Chong: software, data curation. He Li: resources, investigation. Bo Lin: writing – review & editing, funding acquisition, visualization. Guidong Yang: supervision, project administration, writing – review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123474](https://doi.org/10.1016/j.apcatb.2023.123474).

References

- [1] J. Deng, J.A. Iníguez, C. Liu, Electrocatalytic nitrogen reduction at low temperature, *Joule* 2 (2018) 846–856, <https://doi.org/10.1016/j.joule.2018.04.014>.
- [2] Z. Lu, S.E. Saji, J. Langley, Y. Lin, Z. Xie, K. Yang, L. Bao, Y. Sun, S. Zhang, Y.H. Ng, L. Song, N. Cox, Z. Yin, Selective N₂/H₂O adsorption onto 2D amphiphilic amorphous photocatalysts for ambient gas-phase nitrogen fixation, *Appl. Catal. B: Environ.* 294 (2021), 120240, <https://doi.org/10.1016/j.apcatb.2021.120240>.

- [3] Z. Wei, Z. Gu, Y. Zhang, K. Luo, S. Zhao, Phase-separated CuAg alloy interfacial stress induced Cu defects for efficient N₂ activation and electrocatalytic reduction, *Appl. Catal. B: Environ.* 320 (2023), 121915, <https://doi.org/10.1016/j.apcatb.2022.121915>.
- [4] T. Li, S. Han, C. Wang, Y. Huang, Y. Wang, Y. Yu, B. Zhang, Ru-doped Pd nanoparticles for nitrogen electrooxidation to nitrate, *ACS Catal.* 11 (2021) 14032–14037, <https://doi.org/10.1021/acscatal.1c04360>.
- [5] P. Shen, X. Li, Y. Luo, N. Zhang, X. Zhao, K. Chu, Ultra-efficient N₂ electroreduction achieved over a rhodium single-atom catalyst (Rh₁/MnO₂) in water-in-salt electrolyte, *Appl. Catal. B: Environ.* 316 (2022), 121651, <https://doi.org/10.1016/j.apcatb.2022.121651>.
- [6] X. Wang, S. Li, Z. Yuan, Y. Sun, Z. Tang, X. Gao, H. Zhang, J. Li, S. Wang, D. Yang, J. Xie, Z. Yang, Y. Yan, Optimizing electrocatalytic nitrogen reduction via interfacial electric field modulation: elevating d-band center in WS₂-WO₃ for enhanced intermediate adsorption, *e202303794*, *Angew. Chem. Int. Ed.* 62 (2023), <https://doi.org/10.1002/anie.202303794>.
- [7] G. Qian, W. Lyu, X. Zhao, J. Zhou, R. Fang, F. Wang, Y. Li, Efficient photoreduction of diluted CO₂ to tunable syngas by Ni–Co dual sites through d-band center manipulation, *Angew. Chem. Int. Ed.* 61 (2022), e202210576, <https://doi.org/10.1002/anie.202210576>.
- [8] Z. Ma, X. Liu, X. Wang, Z. Luo, W. Li, Y. Nie, L. Pei, Q. Mao, X. Wen, J. Zhong, Manipulating the d-band center enhances photoreduction of CO₂ to CO in Zn₂GeO₄ nanorods, *Chem. Eng. J.* 468 (2023), 143569, <https://doi.org/10.1016/j.cej.2023.143569>.
- [9] R. Gao, L. Pan, H. Wang, X. Zhang, L. Wang, J.-J. Zou, Ultradispersed nickel phosphide on phosphorus-doped carbon with tailored d-band center for efficient and chemoselective hydrogenation of nitroarenes, *ACS Catal.* 8 (2018) 8420–8429, <https://doi.org/10.1021/acscatal.8b02091>.
- [10] M. Jin, R. Ando, M.J. Jellen, M.A. Garcia-Garibay, H. Ito, Encapsulating N-heterocyclic carbene binuclear transition-metal complexes as a new platform for molecular rotation in crystalline solid-state, *J. Am. Chem. Soc.* 143 (2021) 1144–1153, <https://doi.org/10.1021/jacs.0c11981>.
- [11] Q. Wu, W. Yang, X. Wang, W. Zhu, S. Lv, Y. Zhou, T. Chen, S. Liu, W. Li, Z. Chen, Inherent vacancies of compressive Ru nanoparticles accelerate electro-catalytic hydrogen energy conversion, *Appl. Catal. B: Environ.* 335 (2023), 122896, <https://doi.org/10.1016/j.apcatb.2023.122896>.
- [12] M.A. Mushtaq, A. Kumar, G. Yasin, M. Arif, M. Tabish, S. Ibraheem, X. Cai, W. Ye, X. Fang, A. Saad, J. Zhao, S. Ji, D. Yan, 3D interconnected porous Mo-doped WO₃@CdS hierarchical hollow heterostructures for efficient photoelectrochemical hydrogen reduction to ammonia, *Appl. Catal. B: Environ.* 317 (2022), 121711, <https://doi.org/10.1016/j.apcatb.2022.121711>.
- [13] X. Bai, L. Guo, T. Jia, D. Hao, C. Wang, H. Li, R. Zong, Perylene diimide growth on both sides of carbon nanotubes for remarkably boosted photocatalytic degradation of diclofenac, *J. Hazard. Mater.* 435 (2022), 128992, <https://doi.org/10.1016/j.jhazmat.2022.128992>.
- [14] T. Ma, C. Yang, L. Guo, R.A. Soomro, D. Wang, B. Xu, F. Fu, Refining electronic properties of Bi₂MoO₆ by In-doping for boosting overall nitrogen fixation via relay catalysis, *Appl. Catal. B: Environ.* 330 (2023), 122643, <https://doi.org/10.1016/j.apcatb.2023.122643>.
- [15] Y. Kong, H. Kong, C. Lv, G. Chen, Engineering reductive iron on a layered double hydroxide electrocatalyst for facilitating nitrogen reduction reaction, *Adv. Mater. Interfaces* 9 (2022), 2102242, <https://doi.org/10.1002/admi.202102242>.
- [16] W. Tong, B. Huang, P. Wang, Q. Shao, X. Huang, Exposed facet-controlled N₂ electroreduction on distinct Pt₃Fe nanostructures of nanocubes, nanorods and nanowires, *Nat. Sci. Rev.* 8 (2021), <https://doi.org/10.1093/nsr/nwaa088>.
- [17] M. Ma, X. Han, H. Li, X. Zhang, Z. Zheng, L. Zhou, J. Zheng, Z. Xie, Q. Kuang, L. Zheng, Tuning electronic structure of PdZn nanocatalyst via acid-etching strategy for highly selective and stable electrolytic nitrogen fixation under ambient conditions, *Appl. Catal. B: Environ.* 265 (2020), 118568, <https://doi.org/10.1016/j.apcatb.2019.118568>.
- [18] J. Chen, G. Qian, B. Chu, Z. Jiang, K. Tan, L. Luo, B. Li, S. Yin, Tuning d-band center of Pt by PtCo-PtSn heterostructure for enhanced oxygen reduction reaction performance, *Small* 18 (2022), 2106773, <https://doi.org/10.1002/smll.202106773>.
- [19] Y. Zhang, L. Ran, Y. Zhang, P. Zhai, Y. Wu, J. Gao, Z. Li, B. Zhang, C. Wang, Z. Fan, X. Zhang, J. Cao, D. Jin, L. Sun, J. Hou, Two-dimensional defective boron-doped niobic acid nanosheets for robust nitrogen photofixation, *ACS Nano* 15 (2021) 17820–17830, <https://doi.org/10.1021/acsnano.1c01016>.
- [20] D. Gao, B. Xia, C. Zhu, Y. Du, P. Xi, D. Xue, J. Ding, J. Wang, Activation of the MoSe₂ basal plane and Se-edge by B doping for enhanced hydrogen evolution, *J. Mater. Chem. A* 6 (2018) 510–515, <https://doi.org/10.1039/C7TA09982G>.
- [21] F. Xu, D. Wu, Z. Wang, A. Ma, F. Wu, H. Xu, G. Fan, Synergistic effect and high performance of transition metal-anchored boron-doped graphyne electrocatalyst applied in the electroreduction of CO₂ to C₁ products: a DFT study, *Appl. Surf. Sci.* 631 (2023), 157505, <https://doi.org/10.1016/j.apsusc.2023.157505>.
- [22] Y. Chen, K. Yang, B. Jiang, J. Li, M. Zeng, L. Fu, Emerging two-dimensional nanomaterials for electrochemical hydrogen evolution, *J. Mater. Chem. A* 5 (2017) 8187–8208, <https://doi.org/10.1039/C7TA00816C>.
- [23] S. Chen, X. Liu, J. Xiong, L. Mi, X.-Z. Song, Y. Li, Defect and interface engineering in metal sulfide catalysts for the electrocatalytic nitrogen reduction reaction: a review, *J. Mater. Chem. A* 10 (2022) 6927–6949, <https://doi.org/10.1039/D2TA00070A>.
- [24] B. Liu, Y. Zheng, H.-Q. Peng, B. Ji, Y. Yang, Y. Tang, C.-S. Lee, W. Zhang, Nanostructured and boron-doped diamond as an electrocatalyst for nitrogen fixation, *ACS Energy Lett.* 5 (2020) 2590–2596, <https://doi.org/10.1021/acsenergylett.5c02590>.
- [25] H.-B. Wang, J.-Q. Wang, R. Zhang, C.-Q. Cheng, K.-W. Qiu, Y. Yang, J. Mao, H. Liu, M. Du, C.-K. Dong, X.-W. Du, Bionic design of a Mo(IV)-doped FeS₂ catalyst for electroreduction of dinitrogen to ammonia, *ACS Catal.* 10 (2020) 4914–4921, <https://doi.org/10.1021/acscatal.9b02882>.
- [26] H. Li, M. Xia, B. Chong, H. Xiao, B. Zhang, B. Lin, B. Yang, G. Yang, Boosting photocatalytic nitrogen fixation via constructing low-oxidation-state active sites in the nanoconfined spinel iron cobalt oxide, *ACS Catal.* 12 (2022) 10361–10372, <https://doi.org/10.1021/acscatal.2c02282>.
- [27] H. Du, C. Yang, W. Pu, L. Zeng, J. Gong, Enhanced electrochemical reduction of N₂ to ammonia over pyrite FeS₂ with excellent selectivity, *ACS Sustain. Chem. Eng.* 8 (2020) 10572–10580, <https://doi.org/10.1021/acscen.3c00513>.
- [28] L. Gao, C. Guo, M. Zhao, H. Yang, X. Ma, C. Liu, X. Liu, X. Sun, Q. Wei, Electrocatalytic N₂ reduction on FeS₂ nanoparticles embedded in graphene oxide in acid and neutral conditions, *ACS Appl. Mater. Interfaces* 13 (2021) 50027–50036, <https://doi.org/10.1021/acsami.1c00513>.
- [29] S. Erkkeldt, M. Petersson, A. Palmqvist, Alumina-supported In₂O₃, Ga₂O₃ and B₂O₃ catalysts for lean NO_x reduction with dimethyl ether, *Appl. Catal. B: Environ.* 117–118 (2012) 369–383, <https://doi.org/10.1016/j.apcatb.2012.01.031>.
- [30] H. Li, P. Wen, Q. Li, C. Dun, J. Xing, C. Lu, S. Adhikari, L. Jiang, D.L. Carroll, S. M. Geyer, Earth-abundant iron diboride (FeB₂) nanoparticles as highly active bifunctional electrocatalysts for overall water splitting, *Adv. Energy Mater.* 7 (2017), 1700513, <https://doi.org/10.1002/aenm.201700513>.
- [31] H. Xiao, T. Wei, X. Ren, B. Lin, G. Yang, PtS quantum dots/Nb₂O₅ nanosheets with accelerated charge transfer for boosting photocatalytic H₂ production, *Nanoscale* 14 (2022) 12403–12408, <https://doi.org/10.1039/D2NR03112D>.
- [32] B. Lin, G. Yang, L. Wang, Stacking-layer-number dependence of water adsorption in 3D ordered close-packed g-C₃N₄ nanosphere arrays for photocatalytic hydrogen evolution, *Angew. Chem. Int. Ed.* 58 (2019) 4587–4591, <https://doi.org/10.1002/anie.201907112>.
- [33] X. Yan, B. Xu, X. Yang, J. Wei, B. Yang, L. Zhao, G. Yang, Through hydrogen spillover to fabricate novel 3DOM-H₂WO₃/Pt/CdS Z-scheme heterojunctions for enhanced photocatalytic hydrogen evolution, *Appl. Catal. B: Environ.* 256 (2019), 117812, <https://doi.org/10.1016/j.apcatb.2019.117812>.
- [34] J. Wang, B. Huang, Y. Ji, M. Sun, T. Wu, R. Yin, X. Zhu, Y. Li, Q. Shao, X. Huang, A general strategy to glassy M-Te (M = Ru, Rh, Ir) porous nanorods for efficient electrochemical N₂ fixation, *Adv. Mater.* 32 (2020), 1907112, <https://doi.org/10.1002/adma.201907112>.
- [35] Y. Ren, C. Yu, X. Han, X. Tan, Q. Wei, W. Li, Y. Han, L. Yang, J. Qiu, Methanol-mediated electrosynthesis of ammonia, *ACS Energy Lett.* 6 (2021) 3844–3850, <https://doi.org/10.1021/acsenergylett.1c00818>.
- [36] X. Ren, M. Xia, B. Chong, X. Yan, N. Wells, G. Yang, Uniform NiP_x nanospheres loaded onto defective H₂WO₃-y with three-dimensionally ordered macroporous structure for photocatalytic nitrogen reduction, *Appl. Catal. B: Environ.* 297 (2021), 120468, <https://doi.org/10.1016/j.apcatb.2021.120468>.
- [37] Y. Zhao, Y. Zhao, R. Shi, B. Wang, G.I.N. Waterhouse, L. Wu, C. Tung, T. Zhang, Tuning oxygen vacancies in ultrathin TiO₂ nanosheets to boost photocatalytic nitrogen fixation up to 700 nm, *Adv. Mater.* 31 (2019), 1806482, <https://doi.org/10.1002/adma.201806482>.
- [38] N. Zhang, A. Jalil, D. Wu, S. Chen, Y. Liu, C. Gao, W. Ye, Z. Qi, H. Ju, C. Wang, X. Wu, L. Song, J. Zhu, Y. Xiong, Refining defect states in W₁₈O₄₉ by Mo doping: a strategy for tuning N₂ activation towards solar-driven nitrogen fixation, *J. Am. Chem. Soc.* 140 (2018) 9434–9443, <https://doi.org/10.1021/jacs.8b02076>.
- [39] M. Wang, S. Liu, H. Ji, T. Yang, T. Qian, C. Yan, Salting-out effect promoting highly efficient ambient ammonia synthesis, *Nat. Commun.* 12 (2021) 3198, <https://doi.org/10.1038/s41467-021-00526-6>.
- [40] L. Zhang, H. Zhou, X. Yang, S. Zhang, H. Zhang, X. Yang, X. Su, J. Zhang, Z. Lin, Boosting electroreduction kinetics of nitrogen to ammonia via atomically dispersed Sn protuberance, *Angew. Chem. Int. Ed.* 62 (2023), e202217473, <https://doi.org/10.1002/anie.202217473>.
- [41] X. Guo, J. Gu, S. Lin, S. Zhang, Z. Chen, S. Huang, Tackling the activity and selectivity challenges of electrocatalysts toward the nitrogen reduction reaction via atomically dispersed Biatom catalysts, *J. Am. Chem. Soc.* 142 (2020) 5709–5721, <https://doi.org/10.1021/jacs.9b13349>.
- [42] J.-C. Liu, X.-L. Ma, Y. Li, Y.-G. Wang, H. Xiao, J. Li, Heterogeneous Fe₃ single-cluster catalyst for ammonia synthesis via an associative mechanism, *Nat. Commun.* 9 (2018) 1610, <https://doi.org/10.1038/s41467-018-03795-8>.
- [43] G. Zhou, T. Li, R. Huang, P. Wang, B. Hu, H. Li, L. Liu, Y. Sun, Recharged catalyst with memristive nitrogen reduction activity through learning networks of spiking neurons, *J. Am. Chem. Soc.* 143 (2021) 5378–5385, <https://doi.org/10.1021/jacs.0c12458>.
- [44] Y. Li, J. Li, J. Huang, J. Chen, Y. Kong, B. Yang, Z. Li, L. Lei, G. Chai, Z. Wen, L. Dai, Y. Hou, Boosting electroreduction kinetics of nitrogen to ammonia via tuning electron distribution of single-atomic iron sites, *Angew. Chem. Int. Ed.* 133 (2021) 9160–9167, <https://doi.org/10.1002/ange.202100526>.
- [45] L. Li, W. Yu, W. Gong, H. Wang, C.-L. Chiang, Y. Lin, J. Zhao, L. Zhang, J.-M. Lee, G. Zou, Sulfur-induced electron redistribution of single molybdenum atoms promotes nitrogen electroreduction to ammonia, *Appl. Catal. B: Environ.* 321 (2023), 122038, <https://doi.org/10.1016/j.apcatb.2022.122038>.
- [46] K. Hu, P. Qiu, L. Zeng, S. Hu, L. Mei, S. An, Z. Huang, X. Kong, J. Lan, J. Yu, Z. Zhang, Z. Xu, J.K. Gibson, Z. Chai, Y. Bu, W. Shi, Solar-driven nitrogen fixation catalyzed by stable radical-containing MOFs: improved efficiency induced by a structural transformation, *Angew. Chem. Int. Ed.* 59 (2020) 20666–20671, <https://doi.org/10.1002/anie.202009630>.
- [47] D. Malko, A. Kucernak, Kinetic isotope effect in the oxygen reduction reaction (ORR) over Fe-N/C catalysts under acidic and alkaline conditions, *Electrochem. Commun.* 83 (2017) 67–71, <https://doi.org/10.1016/j.elecom.2017.09.004>.

- [48] P. Liu, Y. Zhao, R. Qin, S. Mo, G. Chen, L. Gu, D.M. Chevrier, P. Zhang, Q. Guo, D. Zang, B. Wu, G. Fu, N. Zheng, Photochemical route for synthesizing atomically dispersed palladium catalysts, *Science* 352 (2016) 797–800, <https://doi.org/10.1126/science.aaf5251>.
- [49] L. Yang, C. Cheng, X. Zhang, C. Tang, K. Du, Y. Yang, S.-C. Shen, S.-L. Xu, P.-F. Yin, H.-W. Liang, T. Ling, Dual-site collaboration boosts electrochemical nitrogen reduction on Ru-S-C single-atom catalyst, *Chin. J. Catal.* 43 (2022) 3177–3186, [https://doi.org/10.1016/S1872-2067\(22\)64136-6](https://doi.org/10.1016/S1872-2067(22)64136-6).
- [50] R. Liu, H. Fei, J. Wang, T. Guo, F. Liu, J. Wang, Z. Wu, D. Wang, Insights of active sites separation mechanism for highly efficient electrocatalytic N_2 reduction to ammonia over glucose-induced metallic MoS_2 , *Appl. Catal. B: Environ.* 337 (2023), 122997, <https://doi.org/10.1016/j.apcatb.2023.122997>.